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(57) Abstract

Formation of gas hydrate e.g. crystalline hydrates from natural gas, is inhibited or retarded by addition to a medium susceptible thereto of an additive, which is at least one of (i) a hydrophilic colloid, (ii) a cyclic compound with at least -(C=O)-O- group in a ring and (iii) an amino carbohydrate and preferably at least one of (iv) an amino acid or derivative thereof, (v) an amino alcohol or derivative thereof, (vi) a glycol ether or derivative thereof, (vii) a hydroxyacid or derivative thereof, (viii) a corrosion inhibitor and (ix) a polymer of an ethylenically unsaturated compound.

HYDRATE INHIBITION

The present invention relates to hydrate inhibitors and a method for inhibiting the formation of hydrates in particular to a method for inhibiting the formation of hydrates in the petroleum and natural gas industries.

Hydrates are formed of two components, water and certain gas molecules, e.g. alkanes of 1-4 carbons, especially methane and ethane, such as those found in natural gas. These 'gas' hydrates will form under certain conditions, i.e. when the water is in the presence of the gas and when the conditions of high pressure and low temperature reach respective threshold values. The gas may be in the free state or dissolved in a liquid state, for example, as a liquid hydrocarbon.

The formation of such hydrates can cause problems in the petroleum oil and natural gas industries.

Hydrate formation in the field may cause blocked pipelines, valves and other process equipment.

The problem is particularly of concern as natural gas and gas condensate resources are discovered where operating conditions surpass these threshold values, i.e. in deep cold water and on-shore in colder climates.

Hydrates can also form in association with the underground hydrocarbon reservoir thus impeding production by blockage of reservoir pores.

The problem of hydrate formation is however commonest during gas transportation and processing, the solid hydrate precipitating

from moist gas mixtures. This is particularly true with natural gas which when extracted from the well is normally saturated with water. Often in such a case, in a cold climate, hydrates will form in downstream transportation networks and this can cause large pressure drops throughout the system and reduce or stop the flow of natural gas.

Hydrate formation may also occur during natural gas cryogenic liquefaction and separation.

A typical situation where hydrate formation can occur is in offshore operations where produced fluids are transported in a long vertical pipeline, for example, a riser system. Such produced fluids normally include light gases known to form hydrates and water. In such a situation a temperature of 4.5ºC and a pressure of 150 psi would be sufficient for hydrate formation.

Several methods are known to prevent hydrate formation and subsequent problems in pipelines, valves and other processing equipment.

Physical methods have been used, e.g. increasing gas temperature in the pipeline, drying the gas before introduction into the pipeline, or lowering the gas pressure in the system. However, these techniques are either expensive or are undesirable because of loss of efficiency and production.

Chemical procedures have also been used. Electrolytes, for example, ammonia, aqueous sodium chloride, brines and aqueous sugar solutions may be added to the system.

Alternatively, the addition of methanol or other polar organic substances, for example, ethylene glycol or other glycols may be used. Methanol injection has been widely used to inhibit hydrate formation. However, it is only effective if a sufficiently high concentration is present since at low concentrations there is the problem of facilitation of hydrate formation. Also for methanol to be used economically under cold environmental conditions there must be early separation and expulsion of free water from the well in order to minimise

methanol losses in the water phase.

We have now found certain additives which may be used as effective hydrate inhibitors at low concentrations.

Thus, according to the present invention, there is provided a method for inhibiting or retarding hydrate formation, which method comprises adding an additive (hereinafter called the Additive) which is at least one of (i) a hydrophilic colloid (ii) a cyclic compound with at least one -(C=O)-O- group in a ring, and (iii) an amino carbohydrate, and preferably also at least one of (iv) an amino acid or derivative thereof, (v) an amino alcohol or derivative thereof, (vi) a glycol ether or derivative thereof (vii) a hydroxy acid or a derivative thereof, and (viii) a corrosion inhibitor and (ix) a polymer of an ethylenically unsaturated compound, the Additive being added in an amount effective to inhibit or retard hydrate formation, to a medium susceptible to hydrate formation.

The hydrophilic colloid is an organic solid which is soluble in boiling water, e.g. to at least 10 g/l or dispersible in boiling water and may be soluble (at least 10 g/l) or dispersible in water at 20°C. It usually absorbs water strongly, e.g. to at least three times such as 3-15 times its weight of water at 20°C, and swells in water. It can form a colloidal solution or dispersion in water and may have an average molecular weight of at least 10,000, e.g. 100,000-10,000,000. It may be a polysaccharide, e.g. with at least 4 carbohydrate units, especially one with at least some galactose units, e.g. 20-60% of such units, and may contain carboxylic acid residues, so that an aqueous solution or dispersion thereof can have an acidic reaction. The polysaccharide may be a natural gum, e.g. guar, agar, arabic, locust bean, karaya, carob or tragacanth gum, or a cellulosic material, such as starch, which may be unmodified or modified as an alkyl ether, e.g. methyl or ethyl cellulose or hydroxyalkyl ether, e.g. hydroxyethyl cellulose or carboxy alkylated starch, e.g. carboxy methyl cellulose (CMC). The polysaccharide may also be a synthetic, e.g. biosynthetic gum, the

result of a microbiological process, e.g. fermentation; xanthan gum, which can be made by fermentation of dextrose with Xanthomonas campestris cultures is preferred, especially water soluble versions of xanthan gum. The colloid may also be proteinaceous, in particular gelatin or carrageenan (a seaweed extract), e.g. x-carrageenan. The colloid may also be a polyuronic acid or salt thereof, e.g. sodium or ammonium salt or ester thereof, such as a hydroxy alkyl ester (e.g. of propylene glycol), especially with beta-D-mannuronic acid residues; alginic acid and especially sodium alginate is preferred.

Additive (ii) is a cyclic compound with at least one -(C=O)-O- group in a ring. Such additives are usually cyclic lactones or carbonate esters, preferably with 4-8 atoms in total in the ring containing the -(C=O)-O group. The additives are preferably of formula $-R^6-O_a(C=O)-O-$, where a is 0 or 1 and R^6 is a divalent organic group especially with at least one chain of carbon atoms, whose terminal members are bonded to the $-(O)_a(C=O)-O-$ group. The group R^6 is preferably a hydrocarbyl group, e.g. of 2-20 carbons, especially 2-8 carbons. R^6 may be an alkylene group of 2-10 carbons, preferably forming with the $-(O)_a(C=O)-O-$ group a 4-8, especially 6 or 7 membered ring in particular in lactones; Group R^6 is especially an alkylene group with one terminal CH_2 group, in particular that attached to the non carbonyl oxygen atom in a lactone, but preferably group R^6 is an alkylene group with 2 terminal CH_2 groups R^6 may be 1,2 ethylene, 1,3 propylene, 1,4 butylene, 1,4-pentylene, 1,5-pentylene and 6-methyl-1,5-pentylene. R^6 may also be cycloalkylene group e.g. of 5-7 carbons especially a 1,2-cycloalkylene group, such as cyclohexylene, or an alkylenecycloalkylene group or alkylenecycloalkylene alkylene group, each preferably of 5-10 carbons with 1-3 carbons in the or each alkylene group; examples of such groups are 1,2-cyclohexylene, and 2-methylene,1-cyclohexylene and cyclohexane 1,2-methylene, R^6 may also be a divalent aromatic group e.g. of 6-10 carbons such as a divalent hydrocarbyl group e.g. 1,2-phenylene or an alkylene aromatic group or alkylene aromatic alkylene group,

with the or each alkylene group of 1-3 carbons and the aromatic group as defined above, examples being 1-phenylene 2-methylene and phenyl 1,2-bismethylene. If desired the group R^6 may be attached to a hydrocarbyl polymer with the or each $-O_a(C=O)-O-$ group present as part of a ring, pendant on or fused to the hydrocarbyl polymer chain. The rings usually have 5-8 ring atoms. The above groups R^6 may be unsubstituted by any non hydrocarbylsubstituents, and any alkyl chains present are usually of less than 8 e.g. less than 4 carbons.

Examples of the cyclic compounds which are lactones are propiolactone, gamma butyrolactone, gamma valerolactone, 6-caprolactone and the lactone of 2-hydroxymethyl benzoic acid, while examples of the cyclic carbonates are those from ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,2 and 1,3-butanediols, cyclohexane 1,2-diol and o-catechol, though polyvinyl carbonate may also be used e.g. that derived from "polyvinyl alcohol" (formed by hydrolysis of polyvinyl acetate).

Additive (iii) is an amino carbohydrate in which an amino group is preferably a secondary or especially primary amino group (NH_2), especially the additive containing at least 1 amino group per carbohydrate ring. The amino group is usually bonded directly to a carbon atom in the carbohydrate ring or is separated therefrom by a carbon atom e.g. as in an amino methyl carbohydrate. The Additive contains at least one carbohydrate ring which may be a pentose or especially a hexose ring, and the amino group is especially a 2-amino group in the ring. Examples of such amino carbohydrates are glycosamine and fructosamine, as well as polymers thereof such as chitosan, (polyglucosamine, formed by enzymic hydrolysis of chitin); the polymers may have molecular weights of 10,000 to 5 million e.g. 30,000-200,000 or 100,000-5 million such as 500,000 to 3 million.

The Additives (i), (ii) or (iii) may be used above or mixed with each other or preferably mixed with at least one of the additives (iv)-(viii), especially (viii).

The Additive (iv)-(vii) (and often viii) is usually at least

difunctional, e.g. with 2-4 functional groups. It preferably has a structure including an oxygen atom in an ether group or hydroxyl group and at least one of another oxygen atom in an ether or keto group and a nitrogen atom in an amino group, said O and N and/or O atoms being spaced by 1-6, preferably 2-5, especially 2 or 3 carbon atoms, which may be in an aliphatic, cycloaliphatic or aromatic group.

The Additive (iv) may be an amino acid or derivative thereof, in particular one with at least one asymmetric carbon atom; the Additive may be in the racemic form, but is preferably optically active, i.e. in D or especially L-form. The Additive (iv) may be in the form of the free carboxylic acid (including a carboxylic anion form, e.g. as a sodium or potassium salt) or as a derivative of said carboxylic acid, e.g. as an amide (e.g. with ammonia or with a primary amine which may or may not be a hydroxyamine) or hydrazide (e.g. with hydrazine) or an ester, e.g. as an alkyl ester, e.g. with 1-6 carbons such as a methyl or ethyl ester, or a hydroxyalkyl ester, e.g. with 1-6 carbons such as hydroxymethyl, 1 or 2 hydroxyethyl, 2 or 3 hydroxypropyl ester. The amino acid (or derivative) is preferably an alpha amino carboxylic acid, especially with the amino and carboxylic acid groups bonded to an aliphatic carbon atom, especially a -CH- group. The amino group in the amino acid may also be in a non alpha position relative to the acidic group, e.g. in a beta, gamma or delta position, especially terminal on an alkyl, phenyl or phenylalkyl group attached to the acidic group; examples are omega amino alkanoic acids such as 4-amino butyric acid and p-amino phenyl acetic acid. Iminodiacetic and N-hydroxy methyl iminodiacetic acid may also be used. The Additive may contain an amino group in NH_2 or NH_3 form (whether as a salt, e.g. hydrochloride or hydrobromide or zwitter ion form) or an N-acyl derivative thereof, such as with an alkanoic acid, e.g. of 1-10 carbons such as acetic acid, or an aromatic acid, e.g. of 6-16 carbons such as benzoic acid or a carbonate half ester such as a monoalkyl carbonate, e.g. mono tert butyl carbonate or an aromatic

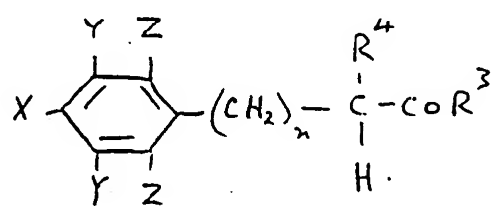
or aralkyl carbonate, e.g. phenyl carbonate or benzyl carbonate. Derivatives of the amino acid with an N-hydroxy alkyl group, e.g. of 1-4 carbons, e.g. 1 or 2 carbons such as hydroxymethyl may also be used; such derivatives may also involve an NH ring in which the hydroxy 1 and acid groups are substituents as in hydroxy proline. Examples of such amino acid derivatives with an N-hydroxy alkyl group are N-sulphoalkyl and N-carboxyalkyl derivatives of Additives (v) as further described below; such compounds may be 1, 2 or 3 sulphoalkylene or especially 1,2 or 3 carboxyalkylene derivatives, especially linear alkylene derivatives. Especially preferred are those derivatives which are N-derivatives of a tris(hydroxyalkyl) alkylamine, in particular tris(hydroxymethyl) methylamine, such as N-[(tris hydroxymethyl)methyl] glycine.

The Additive (iv) is however preferably of formula (I) R-$CH(NH_2)COOH$ (or a derivative thereof), wherein R represents hydrogen or an aromatic, aralkyl, heterocyclic, heterocyclic aliphatic, cycloaliphatic or aliphatic group. The aromatic group preferably has 6-20 carbons, e.g. 6-10 carbons, such as phenyl optionally substituted by amino, hydroxyl carboxylic or alkyl, e.g. of 1-6 carbons such as methyl or ethyl or alkoxy, e.g. of 1-6 carbons such as methoxy or ethoxy. The aralkyl group preferably comprises an aromatic group as described above and the alkyl part of the aralkyl group preferably has 1-4 carbons such as methyl or 1 or 2 ethyl. The heterocyclic ring in the heterocyclic or heterocyclic alkyl group may be a nitrogen heterocyclic ring with 1-3 ring nitrogens as in a 1,3-imidazole ring. The cycloaliphatic group may have 5-8 carbons, e.g. cyclohexyl or cyclopentyl. The group R is especially an aliphatic group, e.g. of 1-6 carbon atoms, in particular a saturated hydrocarbyl group, e.g. linear or branched and optionally substituted, especially in a terminal position in the hydrocarbyl group by at least one of a hydroxyl, alkoxy, mercapto or alkyl thio group, e.g. with 1-6 carbons, especially 1 or 2 carbons in the alkoxy and alkyl thio group, or an amino group, e.g. of formula $-NR^1R^2$, wherein each of R^1 and R^2 which may be the same or different represents hydrogen or alkyl of

1-6 carbons such as methyl or ethyl, or may be an NHC = NH- (NH_2) group (as such or in a salt form) or a ureido or carboxylic acid group or ester (e.g. alkyl or hydroxyalkyl ester) or hydrazide or amide thereof.

Thus the amino acid which is the Additive (iv) or from which it is derived, may be a basic amino acid with 2 or 3 amino groups and 1 carboxylic acid group, such as ornithine, lysine, arginine or guanidine or histidine, especially in its L-form, or an acidic amino acid with 2 or 3 carboxylic acid groups and 1 amino group, such as glutamic or aspartic acid or amide, especially in its L-form. Most preferably, however, the amino acid, which the Additive (iv) is or from which it is derived, has 1 amino and 1 carboxylic group (or derivative thereof) especially one of formula I, in which R is alkyl or hydroxyalkyl, alkoxyalkyl, mercaptoalkyl or alkylmercaptoalkyl group or in the case of mercaptoalkyl groups (as in cysteine) the corresponding disulphide (as in cystine); such amino acids are preferably in their L forms. The Additive is thus preferably serine, threonine, valine, leucine, isoleucine, homoserine, methionine, cysteine or cystine; L-serine is preferred.

The Additive of formula 1 may also be of formula II



where R^3 is OH, OCH_3, OC_2H_5, $NHNH_2$ or H, R^4 is NH_2 or NH_3, each of X, Y and Z is hydrogen or OH and n is a number in the range 0 to 6, or a polymer thereof when R^3 is NH_2, and may be phenylalanine or tyrosine or their carboxylic acid derivatives. There may be used compounds of formula II, wherein at least one of X, Y and Z represents an alkoxy, acyloxy, keto, amino or carboxyl group such as an alkoxy group of 1-6 carbons, e.g. methoxy or ethoxy, or acyloxy such as aliphatic acyloxy, e.g. of 1-10 carbons such as

acetoxy, or keto as in alkylketo with 2-6 carbons, e.g. CH_3CO-. Advantageously, however, in the additive of formula I, group R does not comprise an aromatic group.

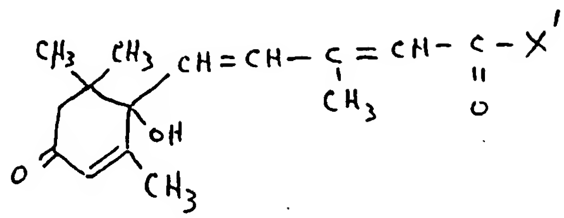
The amino acid may also be an amino sulphonic acid, e.g. with an aliphatic group, e.g. of 1-10 carbons, aromatic group, e.g. of 6-16 carbons or cycloaliphatic group, e.g. of 5-7 carbons, to which the amino and sulphonic groups are attached. Taurine and amino benzene sulphonic acid may be used.

The Additive (v) may also be an hydroxyamine, which is usually an aliphatic compound with 2-10 carbon atoms, especially 3-6 carbon atoms, in particular a saturated aliphatic compound. The Additives (v) may contain 1-5 hydroxyl groups, e.g. 1, 2 or 3 hydroxy groups and 1-3 amino groups, e.g. 1 or 2 amino groups, which may be of formula NR^1R^2, where R^1 and R^2 are as defined above. The Additive (v) may be a secondary or tertiary amine, but is preferably a primary amine, e.g. with 1 NH_2 group, and with 1-3 hydroxyl groups and has especially an alkane group, which may be linear or branched, substituted by such amino and hydroxyl groups which are preferably attached to adjacent carbon atoms. The hydroxyamine may be used as such or in the form of a salt with an inorganic acid, e.g. hydrochloric acid or an organic acid, e.g. an aliphatic mono or di carboxylic acid such as one with 1-10 carbon atoms, e.g. acetic or propionic acid or maleic or oxalic acid or an organic sulphonic acid or organic sulphate half ester, each of which usually contains 1-20 carbons in the organic group, which is preferably a hydrocarbyl group such as alkyl e.g. of 1-8 carbons such as methyl or ethyl especially for the sulphonic acid, or of 1-24 such as 8-22 carbons such as octyl, lauryl and stearyl, especially for the half ester, or may be aryl of 6-20 carbons such as phenyl or tolyl or aralkyl of 7-21 carbons such as benzyl. Examples of such Additives (v) are tris-(2 hydroxyethyl) amine, tyrosinol or valinol (e.g. the L isomer) and especially tris-hydroxymethyl-methylamine $(HOCH_2)_3CNH_2$ and its corresponding ammonium chloride and lauryl sulphate salt.

The Additive (vi) may also be an ether, which contains at

least 1 such as 1-6 ether oxygen atoms and 0-6, e.g. 1 oxygen atoms in a hydroxyl group, the number of ether oxygen atoms being preferably at least the same as and especially 0-3 more than the number of hydroxyl oxygen atoms. Preferably the Additives (vi) are glycol ethers, derived structurally from a diol, e.g. an aliphatic diol of 2-4 carbon atoms such as ethylene glycol or 1,3-propylene glycol, or structurally from a self condensate thereof, e.g. di or triethylene glycol, or mixtures of said diols. One or both hydroxyl groups from such diols (or condensate thereof) may be etherified, e.g. with an alkyl group such as one with 1-10 carbons, e.g. methyl, ethyl, n-propyl or n-butyl. Preferably such Additives (vi) are the reaction products of an alkanol with ethylene oxide and/or propylene oxide. One or more hydroxyl groups in the ether may be acylated, e.g. with an aliphatic or aromatic acyl group with 1-10 or 6-16 carbon atoms respectively such as acetyl or benzoyl. Examples are 2-butoxyethanol (monobutyl glycol ether) and 2(2^1-butoxy ethoxy) ethanol (mono butyldiethylene glycol ether) and their corresponding acetates.

The Additive (vii) is a hydroxy acid (especially a hydroxy carboxylic acid) which may be an aliphatic, aromatic, cycloaliphatic, cycloaliphatic-aliphatic or araliphatic compound with 1-20, 6-20, 5-7, 5-25 or 7-20 carbon atoms respectively. Preferably the aliphatic hydroxy acid is an alpha hydroxy acid, e.g. of 2-6 carbons such as glycollic, lactic or citric acid, while the aromatic and araliphatic acids may be salicylic, p-hydroxybenzoic or 2-(p-hydroxyphenyl) propionic acid. Derivatives of the additive (vii) on the carboxyl group may be used such as salts, e.g. with alkali metals, esters[e.g. with an alcohol with 1 hydroxyl group or with a polyol (though esters from polyols are preferably absent)], amides or hydrazides, in particular when the additive (vii) contains at least one group -COX where X^1 is as defined below. However, preferably the hydroxy acid is a cycloaliphatic-aliphatic compound, especially one with at least one of a keto and an olefinic unsaturated group, in particular abscisic acid or a derivative thereof of formula



wherein X^1 represents OR^5, wherein R^5 is hydrogen or alkyl, e.g. of 1-6 carbons optionally hydroxy substituted, such as methyl, ethyl or 2-hydroxyethyl, or X represents amino (e.g. NH_2) or hydrazido (e.g. $NHNH_2$).

All isomers of the aforementioned abscisic acid derivatives may be suitable for use in the method of the present invention. A preferred compound for use in the present invention is (+/-)-2-cis,4-trans abscisic acid.

The additive (viii) is a corrosion inhibitor, e.g. for steel and usually one suitable for use in anaerobic environments, and is especially a nitrogenous one with 1 or 2 nitrogen atoms. The corrosion inhibitor may be a primary, secondary or tertiary amine, or a quaternary ammonium salt, usually in all cases with at least one hydrophobic group, usually a benzene ring or a long chain alkyl group e.g. of 8-24 carbons; the inhibitor preferably has surfactant activity and especially surface wetting activity. It may be a quaternary ammonium salt, a long chain aliphatic hydrocarbyl N-heterocyclic compound or a long chain amine. The quaternary salt may be an (optionally alkyl substituted) benzyl trialkyl ammonium halide, in particular when at least 1 and especially 1 or 2 alkyl groups is of 1-20, in particular 8-20 carbons such as cetyl and the other alkyl groups are of 1-6 carbons such as methyl or ethyl; examples are benzyl alkyldimethyl ammonium chloride and Benzalkonium chlorides. The aliphatic hydrocarbyl group in the heterocyclic compound usually has 8-24 carbons in the hydrocarbyl group, preferably a linear saturated or mono or diethylenically unsaturated hydrocarbyl group; cetyl-, stearyl and especially oleyl- groups are preferred. The N-heterocyclic compound usually has 1-3 ring N atoms, especially 1

or 2 which usually has 5-7 ring atoms in each of 1 or 2 rings; imidazone and imidazoline rings are preferred. The heterocyclic compound may have the aliphatic hydrocarbyl group on an N or preferably C atom in the ring; the ring may also have an amino-alkyl (e.g. 2-amino ethyl) or hydroxyalkyl (e.g. 2-hydroxyethyl) substituent, especially on an N atom. N-2-aminoethyl-2-oleyl-imidazoline is preferred. The long chain amine usually contains 8-24 carbons and preferably is an aliphatic primary amine, which is especially saturated or mono ethylenically unsaturated; an example is dodecylamine.

Mixtures of Additives (i), (ii) or (iii) with more than one of the same type of any of (iv), (v), (vi), (vii) or (viii) may be used, but also mixtures with ones of different types (iii), (iv), (v), (vi), Vii) and/or (viii), especially mixtures of (i), (ii)or (iii) with (viii) and at least one of (iv), (v), (vi) or (vii). Mixtures of Additive (viii) and at least 2 of Additives (i), (iii), (v) and (ix) are preferred. The mixtures may contain at least 1%, but preferably at least 10% and not more than 90% of each Additive, especially in the form of two component mixtures with 25-75; 75-25 ratios of the two components which are in particular mixtures of (i), (ii) or (iii) with (viii). Such mixtures form another aspect of the invention, so there is also provided a blend which comprises a mixture of at least two Additives (i), (ii), (iii), (iv), (v), (vi), (vii) and/or (viii), so long as it comprises at least one Additive (i), (ii) or (iii). Such blends are primarily for use as gas hydrate inhibitors.

Additives (i-ix) for use as hydrate inhibitors are preferably water soluble, e.g. to at least 10 g/l in water at 20ºC. They may be used undiluted, but preferably are in solution such as aqueous solution, for example, as a solution in brine, or preferably an alcohol, for example, a water miscible one such as methanol or ethanol. Preferably are used Additives i-ix, e.g. (i) with (iv)-(viii) an aqueous solution of which has a pH 1.5-12, e.g. 4-9, either naturally or after adjustment of the pH. Additives (viii) are preferably used in alcoholic solution.

The Additive(s) is suitably injected at concentrations in the range 10 to 20,000 ppm, e.g. 30 to 10,000 ppm, especially 50-1200 ppm based on the total water volume in the medium, in which hydrate formation is to be inhibited, in particular at concentrations in the range 100-700 ppm. The amount of methanol, ethanol, or mono, di or tri ethylene glycol added relative to the total water volume in the medium is usually less than 10%, e.g. less than 5% or 2%, but especially less than 10,000 ppm.

The inhibitors may be injected at normal ambient conditions of temperature and pressure.

It has also been found that blends of at least one Additive (i) (ii) or (iii) and (ix) a polymer of a polar ethylenically unsaturated compound can give synergistic results compared to the ingredients above, so that blends of at least one Additive (iii) and a polyvinyl pyrrolidone, had a gas hydrate inhibition time in a test very many more times than each individually, e.g. at least two times more than the sum of their individual times.

The Additives may thus also be used in formulations which also comprise a polymer of a polar ethylenically unsaturated compound; these Formulations constitute another aspect of the invention.

The polymer of the polar ethylenically unsaturated compound (ix) is usually water soluble (to at least 10 g/l at 20°C) and advantageously has a molecular weight of 1000-1500,000, e.g. 5000-1,000,000, preferably 200,000-1,000,000 and especially 400,000-900,000. The ethylenically unsaturated compound is preferably a vinyl or methyl vinyl group, and the polar group may be an alcohol, carboxylic acid, sulphonic acid or N-heterocyclic group, especially pyrrolidone. Preferred polar compounds are thus vinyl sulphonic acid, acrylic and methacrylic acids and N-vinyl pyrrolidone and "vinyl alcohol". The polymers may be copolymers, but are preferably homopolymers of these polar compounds, especially polyvinyl alcohol (e.g. hydrolysed polyvinyl acetate), polyacrylates and polyvinyl pyrrolidone. The amount of said polymer is usually 10-1000%, such as 50-300% or 90-250% based on

the weight of the total of Additive(s) e.g. (i)-(iii) or (iv)-(vii). Blends of the colloid and at least one Additive (iv)-(vii) and/or a polymer of a polar ethylenically unsaturated compound can give synergistic results compared to the ingredients alone, so that blends of at least one Additive (iv)-(vii), the colloid and optionally a polyvinyl pyrrolidone, can have a gas hydrate inhibition time in a test very many more times than each individually, e.g. at least two times more than the sum of their individual times.

Formulations may be used in amount of 50-10,000 ppm, preferably 2000-5000 ppm or 150-2000 ppm, e.g. 500-1500 ppm relative to the total water in the medium in which hydrates may form (including any water added in the formulation). The Formulations may also comprise at least one Additive (iv)-(viii). They may comprise the corrosion inhibitor (Additive (viii)) and the polymer (ix) as well as the Additive (i), (ii) or (iii), which are then preferably in the weight ratio 5-200:100-2000:100-2000, especially 10-100:400-800:150-800 or as percentages of the total formulation weight of corrosion inhibitor, polymer and Additive (i), (ii) or (iii) of 1-20%, 40-80% and 10-60% respectively, especially 1-10%, 40-70% and 20-50% respectively. The Formulations may also comprise the hydrophilic colloid (i) and total Additive (iv)-(viii) in relative amounts of 1:99 to 99.9:0.1, especially 20:80 to 90:10, though the relative amounts of colloid to Additive (viii) are preferably 95:5 to 99:0.5. The relative amounts of colloid (i) to polymer (ix) may be 1:99 to 99:1 such as 10:90 to 90:10 or 30:70 to 70:30. The formulations may comprise (a) the corrosion inhibitor (Additive (viii)), and (b) the colloid (i) alone or with the polymer (ix) as well as the (c) Additive (iv)-(viii), which are then preferably in the weight ratio (a):(b):(c) of 1-200:100-2000:100-2000, especially 2-100:200-800:150-500 or as percentages of the total formulation weight of (a), (b) and (c) of 0.1-20%, 40-80% and 10-50% respectively, especially 0.1-10%, 50-70% and 20-40% respectively. In the Formulation Additive (viii) is usually present in an amount

of 0.1-50% (by weight of the total of Additives (i), (ii) and (iii) or the total of Additives (iv)-(vii), e.g. in either case 1-25%, especially 5-20%.

The Formulation may also contain another hydrate inhibitor and/or a water dispersant or surfactant, in particular an anionic one such as sodium dodecyl sulphonate or stearic acid and in amount of 1-10% of the Formulation weight and/or a biocide, e.g. formaldehyde, e.g. in amount of 10-10,000 ppm and/or a metal complexant such as citric acid (e.g. in amount of 10-10,000 ppm) all amounts being in relation to the total weight of the Formulation.

The Formulations may be used to retard or inhibit hydrate formation in the same manner as the individual Additives, as described above.

The inhibitor Additives and Formulations of the present invention are suitable for use in media containing water and gas, in particular in the petroleum, natural gas and gas industries.

In particular, they may be suitable for use during the transportation of fluids comprising gas and water. They may also be suitable for use in oil based drilling muds to inhibit hydrate formation during drilling operations.

In another aspect therefore the invention provides an oil based drilling mud, which comprises as hydrate inhibitor at least one Additive, as such or in a Formulation.

When used during the transportation of fluids, e.g. gases in pipelines the inhibitors may be injected continuously or batchwise into the pipeline upstream of conditions (e.g. the locus in siad pipeline) wherein hydrate formation may occur, which are often 20-100 bar pressure and -5°C to +6°C.

In drilling operations the inhibitors may be added to the drilling muds in the mud tank at the wellhead.

The invention is illustrated in the following Examples.

Examples

To assess the efficiency of hydrate inhibitors suitable for use in the method of the present invention, tests were carried out using the following procedure:

The hydrate inhibitor test apparatus consisted of a simple 316 stainless steel pressure cell, with a usable internal volume of 1000 cm^3 with a thermostated cooling jacket, a sapphire window, an inlet and outlet and a platinum resistance thermometer. The cell contained water which was stirred by a magnetic pellet. Temperature and pressure were monitored and the results provided on a computer data logger; gas hydrates were also detected visibly using a time lapse video recording system. Before each test the cell was cleaned thoroughly by soaking successively in 10% aqueous hydrochloric acid for 1 hour, 10% aqueous sodium hydroxide solution for 1 hour and then double distilled water.

Into the cell was placed 200 cm^3 of pre-chilled double distilled water with or without the chemical to be tested. A PTFE stirrer pellet was then placed in the cell and the pH of the solution measured with subsequent adjustment if desired by the addition of small but concentrated amounts of hydrochloric acid or sodium hydroxide. After sealing the cell the water was then stirred at 500 rpm and allowed to cool to the operational temperature of 4°C. When this temperature was reached the stirrer was stopped and the video recorder started. Methane was then admitted to the cell until the pressure reached 70 bar and the temperature, pressure and time were noted. The stirrer was restarted to run at 500 rpm and the time noted. Hydrates were observed to form in the vessel when the solution in the vessel turned opaque, coincident with which was a sharp temperature increase of about 0.2°C and a gradual pressure reduction. The time from first contact of water and gas to formation of hydrate was read from the logger.

The experimental conditions are a very severe and accelerated test of gas hydrate formation and inhibition.

Example	Additive	Concentration ppm	pH approx	Inhibition Time (mins)
A	None	-	-	5-9
1	6-Caprolactone	400	5.5	40
2	6-Caprolactone	400	5.5	31
3	6-Caprolactone	500	5.5	78
4	Chitosan HMW	500	5.1	13.5
5	Chitosan HMW	500	5.1	15
6	Chitosan HMW	250	5.0	16
7	Chitosan MMW	500	4.7	21
8	Chitosan LMW	250	5.0	13
9	Chitosan LMW	500	5.0	29.5
10	4-Valerolactone	1000	4.3	16

In the above Table, HMW denotes High Molecular Weight (about 2 million) MMW MediumMolecular Weight (about 750,000) and LMW Low Molecular Weight (about 70,000).

Example 10

The process of Example 4 was repeated with a blend of the following composition Chitosan (HMW) (500ppm), a polyvinyl pyrrolidone of Molecular Weight (Mw) of about 700,000 (from BDH Ltd) (600ppm) and an alkyl benzyl dimethyl ammonium chloride sold as a corrosion inhibitor by Hoechst under the Trade Mark DODIGEN 5462 (50ppm). The pH of the water containing the blend was 4.3. The averaged inhibition time from several experiments was about 115mins.

Examples 11-15

The process of Example 4 was repeated with the Chitosan replaced by the Additives below. The results as follows

Example	Additive	Concentration ppm	pH	Inhibition Time (mins)
A	-	-	-	6
11	Xanthan gum	250	5-6	31
12	Gum arabic	500	5.4	10
13	Gelatin	500	4.8	30
14	x-Carrageenan	500	6.5	15
15	Hydroxyethyl cellulose	500	5.8	16

The additives were obtained from Sigma Chemical.

Example 16

The process of Example 1 was repeated with a Formulation of 250 ppm xanthan gum and also 500 ppm citric acid and 4 ppm of formaldehyde. The Inhibition Time was 20 mins.

Example 17-20

The process of Example 11 was repeated with a Formulation containing Additives as follows.

(A) Xanthan gum, water soluble powder from Sigma Chemical.

Additive (v) B Tris (hydroxymethyl) methyl ammonium hydrochloride

Additive (viii) C alkyl benzyldimethyl ammonium chloride sold by Hoechst under the Trade Mark DODIGEN 5462 as a corrosion inhibitor.

The results were as follows, with an averaged inhibition time from several experiments.

Example	Amount Additive B-C (ppm)		Amount Additive A (ppm)	pH	Inhibition Time (min)
A	-	-	-	-	6
17	-	C 2.5	250	5.6	72
18	-	C 5	500	6.5	34
19	B 350	-	500	5.5	29
20*	B 175	C 2.5	250	3.8	18.5

* Denotes addition also of 40 ppm citric acid.

Examples 21-23

The process of Example 20 was repeated with a Formulation containing Additives (i) A gelatin (500 ppm) (v)B tris(hydroxymethyl) methyl ammonium chloride (700 ppm) and (viii)C the alkyl benzyl dimethyl ammonium chloride DODIGEN 5462, making a total of 1350 ppm Additives. The inhibition time was 154 minutes. The experiment was repeated with the same relative proportion of the Additives A, B and C, but a total amount of 1000 ppm and also 500 ppm, giving averaged inhibition times of 156 and 59 minutes respectively.

Claims:

1. A method for inhibiting or retarding hydrate formation which method comprises adding an Additive, which is at least one of (i) a hydrophilic colloid (ii) a cyclic compound with at least one -(C=O)-O- group in a ring and (iii) an amino carbohydrate, the Additive being added in an amount effective to inhibit or retard hydrate formation, to a medium susceptible to hydrate formation.

2. A method according to claim 1 wherein the Additive (i) is a poly-saccharide gum or gelatin.

3. A method according to claim 2 wherein the Additive (i) is xanthan gum.

4. A method according to claim 1 wherein the Additive (iii) is an amino carbohydrate.

5. A method according to claim 4 wherein the Additive (iii) is chitosan.

6. A method according to any one of the preceding claims which also comprises adding a blend which comprises at least one of Additives (i)-(iii) and at least one of Additives (iv) an amino acid or derivative thereof (v) an amino alcohol or derivative thereof (vi) a glycol ether or derivative thereof (viii) a hydroxyacid or derivative thereof (viii) a corrosion inhibitor and (ix) a polymer of an ethylenically unsaturated compound.

7. A method according to claim 6 wherein Additive (viii) is a Corrosion Inhibitor.

8. A method according to claim 7 wherein the Additive (viii) is a quaternary ammonium salt.

9. A method according to claim 7 or 8 wherein Additive (v) is an amino alcohol.

10. A method according to claim 7, 8 or 9 wherein Additive (i) is a polysaccharide gum.

11. A method according to claim 8 which comprises adding tris(hydroxymethyl)methyl amine (or a salt thereof) and xanthan gum or gelatin.

12. A method according to claim 7 or 8 which comprises adding an amino carbohydrate and a polymer of an ethylenically unsaturated N-heterocyclic compound.

13. A method according to claim 12 which comprises adding chitosan and a polyvinyl pyrrolidone.

14. A formulation for use as a gas hydrate inhibitor which comprises a blend of at least two of Additives (i)-(ix) as defined in claims 1 and 6, so long as it comprises at least one Additive (i), (ii) or (iii).

15. A formulation according to claim 14 wherein the Additives (i)-(ix) are as defined in any one of claims 2-5 and 7-13.

16. A formulation according to claim 14 or 15 which is as defined for the blend in any one of claims 6-13.

17. Method of transporting through a pipeline a fluid comprising water and a gas susceptible to form hydrates, which comprises treating said fluid gas with at least one Additive as defined in any one of claims 1-13 with a formulation as defined in any one of claims 14-16 upstream of a locus in said pipeline wherein gas hydrates may be formed in the absence of said Additive.

18. Use of an Additive as defined in any one of claims 1-5 or a blend as defined in any one of claims 6-13 or a formulation according to any one of claims 14-16 for the inhibition or retardation of the formation of gas hydrates.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/00952

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 E21B37/06 C10L3/00 C09K7/06 F17D1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C10L E21B F17D F15D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 857 686 (ARNOLD ET AL.) 31 December 1974 see the whole document ---	1,17,18
P,X	WO,A,93 25798 (SHELL) 23 December 1993 see page 4 - page 6 ---	1,6,7, 14,16-18
E	WO,A,94 12761 (COLORADO SCHOOL OF MINES) 9 June 1994 see abstract --- -/--	1,6,14, 16-18

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 94/00952

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